# PHOTOCHEMICAL CYCLOADDITION REACTIONS. II.*
# DIMERIZATION AND CYCLOADDUCT FORMATION
# OF SOME SEVEN-MEMBERED CARBOCYCLES

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The photochemical behaviour of 2,3,6,7-dibenzocycloheptatrien-1-one (*I*), 2,3,6,7-dibenzo-cycloheptatriene (*II*) and 1-methylene-2,3,6,7-dibenzocycloheptatriene (*III*), individually and in the presence of each other, was studied. Irradiation of solutions of these substances led to the formation of *anti* cyclobutane dimers and adducts; reactions occurred exclusively at the endo-cyclic olefinic sites in *I* and *III*. This observed photospecifity is supported by MO calculations of delocalization energies for the possible reactive sites in the monomers. The elucidation of structures, thermal decomposition, chemical interconversions, and stereochemistry of all photo-products are described.

In connection with efforts directed toward facile light-induced syntheses of $10\pi$ electron systems, we have investigated the photochemical behaviour of 2,3,6,7-di-benzocycloheptatrien-1-one (*I*), 2,3,6,7-dibenzocycloheptatriene[1] (*II*) and 1-methylene-2,3,6,7-dibenzocycloheptatriene[2] (*III*). This paper describes the synthesis, proper-ties, structural and stereochemical elucidation of all possible photodimers and 1 : 1 cycloadducts arising from irradiation of solutions of these compounds, together with a theoretical correlation of the observed reactivities of compounds *I*, *II* and *III*, with calculated delocalization energies.

*Photochemical synthesis.* Brief irradiation of solutions of dibenzotropone (*I*) in a variety of solvents, *e.g.*, acetone, benzene, cyclohexane, diethyl ether, methanol, led to the formation of only one photoproduct, m.p. $237-238°C$ dec., shown by elemental analysis, molecular weight and spectral properties (see Experimental) to possess structure *IV*.* Yields of *IV* varied with the solvent used, however no correlation between amount of dimer formation and solvent polarity was found. The highest yield (95%) of *IV* was obtained from irradiation of *I* in isopropyl alcohol. It is of interest

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to note that, in contrast to benzophenone, no photoreduction products were observed when $I$ was irradiated in protic solvents. This behaviour suggests that the lowest triplet state of dibenzotropone has $\pi$, $\pi^*$ character, in contrast to the chemically active state $(n, \pi^*)$ of ketones which undergo photoreduction. Further support for this behaviour of $I$ is provided by the low value observed for its triplet state energy $(52 \text{ kcal mol}^{-1})$, which is well below the range observed for good photoreducers $(69-74 \text{ kcal mol}^{-1})$[4]. Similarly, dimer $V$, m.p. $341-342°$C dec., was obtained by irradiation of dibenzotropilidene $(II)$ in cyclohexane solution. Infrared and NMR spectral data are consistent with structure $V$.

Although monomers $I$ and $II$ were found to be readily susceptible to photodimerization, irradiation of dibenzoheptafulvene $(III)$ in various solvents was unproductive. However, three products resulted from the light-induced reaction of a cyclohexane solution containing equimolar amounts of $III$ and dibenzotropone $(I)$. Column chromatographic separation of the crude reaction mixture afforded ketone dimer $IV$ (10%), the desired dimeric hydrocarbon $VI$, (72%) m.p. $247-248°$C dec., and a cycloadduct, m.p. $217-218°$C dec., in 14% yield. The latter photoproduct, on the basis of molecular weight, elemental analysis and spectral data was identified as 1 : 1 adduct $VII$. The yield of $VII$ was raised to 80%, at the expense of dimer $VI$ by the use of a two-fold excess of $I$ in the irradiation.

Encouraged by the results of the mixed cycloaddition leading to $VII$, we turned our attention to the photochemical behaviour of other monomeric mixtures. Thus, irradiation of a solution of an equimolar mixture of $I$ and $II$ in cyclohexane afforded, in addition to the expected photodimers $IV$ and $V$ cycloadduct $VIII$ in 10% yield. However, difficulties were encountered in the isolation of a pure sample of $VIII$, as evidenced by our inability to procure a satisfactory elemental analysis. The complete
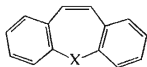


$I$,   X = C=O
$II$,  X = CH$_2$
$III$, X = C=CH$_2$
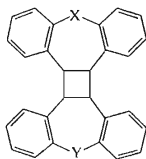
$IV$,   X = Y = C=O
$V$,    X = Y = CH$_2$
$VI$,   X = Y = C=CH$_2$
$VII$,  X = C=O; Y = C=CH$_2$
$VIII$, X = C=O; Y = CH$_2$
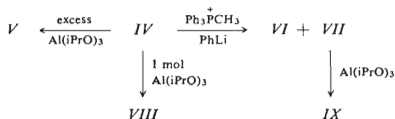$IX$,   X = CH$_2$; Y = C=CH$_2$

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•    Tochtermann and coworkers[3] reported the formation of a dimer of dibenzotropone, but did not elucidate its stereochemistry.

separation of 1 : 1 adduct *VIII* from unreacted dibenzotropone (*I*) could not be accomplished by the usual methods of purification (recrystallization, sublimation, chromatography).

Adduct *IX* was formed in 20% yield, along with dimers *V* (20%) and *VI* (31%) by irradiation of an equimolar mixture of *II* and *III* in cyclohexane solution. Spectral data (see Table I and Experimental) for all photoproducts are consistent with the assigned structures.

*Thermal decomposition.* All photoproducts were found to undergo reversal to their respective progenitors on heating for several minutes at the melting point. Recrystallization of the melts from thermolysis of photodimers *IV*, *V* and *VI* afforded the respective monomers *I*, *II* and *III*, as shown by mixture melting point and infrared spectral comparison with corresponding samples. Thermal reversibility of the photoadducts *VII*, *VIII* and *IX* was verified by thin layer chromatographic analysis of their melts, which indicated essentially complete decomposition of each adduct to a mixture of the two precursory monomers.
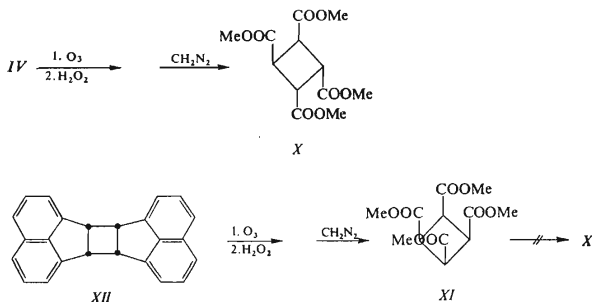
*Elucidation of structure.* Chemical interconversion of photodimers and adducts, by a series of reactions which should not affect the stereochemistry of the cyclobutane ring, serves not only to lend support to the structures proposed herein but also to establish similarities in their geometry. Accordingly, aluminum isopropoxide reduction* of *IV* gave *V* identical in all respects to the photochemically-produced hydrocarbon. In contrast, treatment of *IV* with a limited quantity of this same reducing agent provided an authentic sample of cycloadduct *VIII*, which unfortunately was slightly contaminated by monomer *I*; the latter was apparently formed by thermal decomposition of *IV* at the elevated temperature required for the reduction. Authentic samples of photoproducts *VI* and *VII* were obtained by the Wittig reaction. Thus, treatment of *IV* with methylenetriphenylphosphorane afforded a mixture of *VI* and *VII*, readily separable by chromatography on silica gel. Lastly, the synthesis of 1 : 1 hydrocarbon cycloadduct *IX* was accomplished by reduction of tropone–fulvene adduct *VII* with aluminum isopropoxide. The identities of all photodimers and adduct were established by comparison (melting point, mixture melting point, tlc mobility and spectral data) with the compounds prepared by chemical transformation of diketone *IV*. A summary of these interconversions is shown in Scheme 1.

$$V \xleftarrow[\text{Al(iPrO)}_3]{\text{excess}} IV \xrightarrow[\text{PhLi}]{\text{Ph}_3\overset{+}{\text{P}}\text{CH}_3} VI + VII$$

$$\downarrow \begin{smallmatrix} \text{1 mol} \\ \text{Al(iPrO)}_3 \end{smallmatrix} \qquad\qquad \downarrow \text{Al(iPrO)}_3$$

$$\text{Scheme 1} \qquad\qquad VIII \qquad\qquad\qquad IX$$

* N. L. Wendler, D. Taub and R. D. Hoffsommer[5] employed this method for the reduction of *I* to *II*.

*Stereochemistry.* The observed interconvertibility of photodimers and adducts establishes that all photoproducts possess the same geometry. The assignment of *anti* stereochemistry to these compounds was made by oxidative degradation of diketone *IV* to a known *trans* cyclobutane derivative. A suspension of *IV* in aqueous acetic acid was treated with ozone at room temperature. Oxidative decomposition of the ozonide, followed by esterification of the crude tetraacid with diazomethane afforded after chromatography *cis,trans,cis*-1,2,3,4-tetracarbomethoxycyclobuta-ne[6] (*X*).

$$IV \xrightarrow[\text{2.H}_2\text{O}_2]{\text{1. O}_3} \xrightarrow{\text{CH}_2\text{N}_2}$$

COOMe
MeOOC
COOMe
COOMe

*X*



$$XII \xrightarrow[\text{2.H}_2\text{O}_2]{\text{1. O}_3} \xrightarrow{\text{CH}_2\text{N}_2} \xrightarrow{/\!\!/} X$$

COOMe
MeOOC   COOMe
MeOOC

*XI*

Evidence that compound *X* possesses the stereochemical configuration of dimer *IV* and that *X* was not formed in the oxidative degradation process by isomerization of the *cis* form *XI* was obtained as follows. *cis,cis,cis*-1,2,3,4-Tetracarbomethoxy-cyclobutane (*XI*)* was subjected to identical reaction and purification conditions used in the preparation and isolation of *X*; no isomerization of *XI* to *X* was observed.

The *trans* geometry of photoproducts was further confirmed by comparison of their NMR spectra (see Table I) with those of a number of known photodimers, whose stereochemistry has been established.

The NMR chemical shifts of cyclobutane protons presented in Table I provide a sufficient number of examples to serve as a means of assigning stereochemical configuration to cyclobutyl derivatives. Thus, the *syn* cyclobutane dimers *XII* and *XIV* exhibit lower field absorption ($\tau$ 5·1−5·4) than the analogous *anti* dimers, *XIII* and *XV* ($\tau$ 5·8−6·0). In agreement with this generalization, the *anti* photoproducts (*IV−IX*) described in this paper all exhibit absorption at the higher field ($\tau$ 5·5−6·0). The *syn* geometry of β-heptacyclene (*XII*), the *cis* photodimer of acenaphthylene, corresponds to cyclobutane proton absorption of $\tau$ 5·1−5·3. In contrast the *trans*

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\*      Tetraester *XI* was prepared by ozonolysis of β-heptacyclene (*XII*)[7].

TABLE I
NMR Chemical Shifts of Cyclobutane Protons

| Compound | Chemical shift (TMS-τ) | Solvent |
|----------|------------------------|---------|
| IV | 5·95[a] (s) | CDCl$_3$ |
| V | 5·50 (s) | CDCl$_3$ |
| VI | 5·75 (s) | CDCl$_3$ |
| VII | 5·80[a] (m) | CDCl$_3$ |
| VIII | 5·77 (m) | CDCl$_3$ |
| IX | 6·00 (m) | C$_6$D$_6$ |
| XII | 5·3[b] (s) | CD$_2$Cl$_2$ |
|  | 5·10[c] (s) | DMSO-d$_6$ |
| XIII | 6·0[b] (s) | CD$_2$Cl$_2$ |
|  | 5·91[c] (s) | DMSO-d$_6$ |
| XIV | 5·40[c] (s) | DMSO-d$_6$ |
| XV | 5·80[d] (s) | CDCl$_3$ |

[a] s Singlet; m multiplet. [b] Ref.[8]. [c] Ref.[9] [d] Ref.[10].

dimer, α-heptacyclene (XIII)* exhibits this proton absorption upfield at τ 6·0. Schönberg[9] assigned the *syn* configuration to compound XIV, the photodimer of 2,3,6,7—2′,3′,6′,7′-tetrabenzoheptafulvene on the basis of the unusual spatial requirements imposed by the formation of two cyclobutane rings; dimer XIV shows cyclobutane proton absorption at τ 5·4. Sasse[10] has suggested a *trans* cyclobutane structure for compound XV, a photodimer of 4H-cyclopenta(d,e,f)phenanthrene, based on the observed similarity in the chemical shifts of the cyclopentyl methylene protons in the monomer and dimer; shielding of these protons would be expected if the configuration of XV were *syn*. Compound XV exhibits absorption at τ 5·8 in accord with an *anti* stereochemistry.

*Theoretical discussion of photoreactivity.* The success achieved by Fukui[12] and Nagata[13], who used a molecular orbital approach to reactivities in the photodimerization of some aromatic compounds, prompted us to correlate the observed photoreactivities of I, II and III with the calculated π-delocalization energies for all possible reactive sites in each monomer, designated by the numbering shown in Scheme 2.**

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\*      Photodimer XIII of acenaphthylene was shown by X-ray diffraction to possess *trans* orientation[11].

\*\*     Fukui[12] has derived equations for the calculation of π-delocalization energies for excited molecules and has shown that the magnitude of this reactivity index parallels the molecules ability to react photochemically.
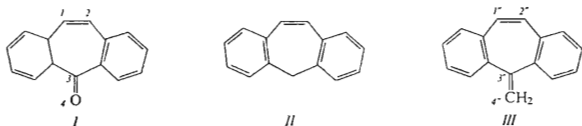
SCHEME 2

TABLE II

Comparison of Delocalization Energy with Photo-Dimer and Adduct Forming Ability

| Compound | Position of photo-product formation | Delocalization energy[a] | Photoproduct formation[b] |
|----------|-------------------------------------|--------------------------|---------------------------|
| I—I      | 1—1, 2—2                            | 0·5256                   | +                         |
|          | 1—3, 2—4                            | 0·1223                   | —                         |
| I—II     | 1—1′, 2—2′                          | 0·5340                   | +                         |
|          | 3—1′, 4—2′                          | 0·1264                   | —                         |
| I—III    | 1—1″, 2—2″                          | 0·4760                   | +                         |
|          | 3—1″, 4—2″                          | 0·0959                   | —                         |
|          | 1—3″, 2—4″                          | 0·3246                   | —                         |
|          | 3—3″, 4—4″                          | 0·1370                   | —                         |
|          | 3—4″, 4—3″                          | 0·0841                   | —                         |
| II—II    | 1′—1′, 2′—2′                        | 0·5428                   | +                         |
| II—III   | 1′—1″, 2′—2″                        | 0·4818                   | +                         |
|          | 1′—3″, 2′—4″                        | 0·3356                   | —                         |
| III—III  | 1″—1″, 2″—2″                        | 0·4428                   | +                         |
|          | 1″—3″, 2″—4″                        | 0·2547                   | —                         |
|          | 3″—3″, 4″—4″                        | 0·3590                   | —                         |
|          | 3″—4″, 4″—3″                        | 0·1139                   | —                         |

[a] Coulomb and resonance integrals for compound I were taken from ref.[14]. Delocalization energies are given in $-\beta$ units. [b] + and — refer to product and lack of product, respectively.

Table II gives the calculated π-delocalization energies (DE) of all possible photo-dimers and adducts from compounds I, II, and III together with the observed products from the various combinations of monomers. The second column shows the various possible pairing of positions which might be expected to react photochemically, e.g. photodimerization of dibenzotropone (I—I) could, in theory, occur by pairing either

of positions $1-1$ and $2-2$ or of positions $1-3$ and $2-4$. A definite parallelism was found between the magnitude of the DE and the type of product observed in the photoreaction. In all cases, the position-pairing having the largest DE value led to product formation. Accordingly, no oxetane product was observed from the irradiation of $I$; exclusive formation of dimer $IV$ can be predicted from a comparison of the DE values, i.e., 0·5256 and 0·1223 for cyclobutane and oxetane formation, respectively. Similarly, the failure to observe photoproducts resulting from reaction at the exocyclic double bond in $III$ is predictable from the magnitude of the DE values involving this position $(3''-4'')$ compared to those involving the endocyclic site $(1''-2'')$.

The experimental dimer-forming ability of compounds $I$, $II$ and $III$ was also found to be in accord with the delocalization energy values calculated for the appropriate monomer combinations i.e., $I-I$, $II-II$ and $III-III$. Thus, monomers $I$ and $II$ underwent facile conversion to their respective dimers; the necessary position combinations have relatively high DE values (0·5256 and 0·5428, respectively). On the other hand, photodimer $VI$ was obtained only by irradiation of $III$ in the presence of a sensitizer, a result which is in agreement with the smaller DE value (0·4428).

## EXPERIMENTAL

Irradiations were made with a Phillips 125 W high pressure mercury lamp suspended in a quartz reaction vessel. A Solidex filter was placed between the lamp and the reaction solution and the temperature maintained at $20 \pm 5°C$ by means of water circulation through the apparatus. All solutions were flushed with nitrogen for 15 minutes before irradiation. Melting points are uncorrected. Thin layer separations were made on silica gel (with fluorescent indicator) as adsorbent. Infrared spectra, obtained from KBr pellets, were recorded on a Perkin-Elmer Model 137 Infracord. Nuclear magnetic resonance spectra were determined with Varian Model A-60 and T-60 spectrometers with tetramethylsilane as internal standard. Elemental analyses were performed by Chemalytics, Inc., Tempe, Arizona and Galbraigth Laboratories, Inc., Knoxville, Tennessee. Molecular weights were obtained by vapor pressure osmometry.

*Photodimer of dibenzotropone (IV).* A solution of 1·0 g of $I$ in isopropyl alcohol (125 ml) was irradiated for 1·5 h. Filtration of the white precipitate furnished 0·95 g (95%) of dimer $IV$, m.p. 237—239°C dec. (lit.[3] m.p. 237—238·5°C dec.); IR (KBr) 1 655 cm$^{-1}$ (C=O); NMR (CDCl$_3$) $\delta$ 4·1 (s, 4, cyclobutane H), 6·3 (m, 16, aromatic H). Recrystallization of the crude dimer from 95% ethanol gave 0·8 g of $IV$ as colorless plates, m.p. 238·5—239°C dec. For C$_{30}$H$_{20}$O$_2$ (411·5) calculated: 87·36% C, 4·89% H; found: 87·56% C, 4·78% H, m.w. 417.

*Photodimer of 2,3,6,7-dibenzocycloheptatriene (V).* Irradiation of a solution of 300 mg of $II$ in cyclohexane (125 ml) for 6 h led to the precipitation of 147 mg of $V$; concentration of the filtrate gave a further 94 mg of dimer; m.p. 330—340°C dec. Recrystallization from toluene furnished an analytical sample of $V$, m.p. 341—342°C dec.; NMR (CDCl$_3$) $\delta$ 7·0 (m, 16, aromatic H), 4·5 (s, 4, cyclobutane H), 4·8 (s, 4, methylene H).

For C$_{30}$H$_{24}$ (384·5) calculated: 93·71% C, 6·29% H; found: 93·54% C, 6·42% H, m.w. 380.

*Photodimer of 1-methylene-2,3,6,7-dibenzocycloheptatriene (VI).* A solution containing 312 mg (1·5 mmol) of dibenzotropone ($I$) and 309 mg (1·5 mmol) of 1-methylene-2,3,6,7-dibenzocyclo-heptatriene ($III$) in cyclohexane (125 ml) was irradiated for 6 h. Chromatography of the resulting

solution on a column of silica gel, using in succession hexane and hexane–benzene mixtures as eluants, gave 32 mg (10%) of ketone dimer *IV*, 43 mg (14%) of cycloadduct *VII* and 220 mg (72%) of hydrocarbon dimer *VI*, m.p. 235—240°C dec. Recrystallization of the dimer from ligroin afforded an analytical sample of the dimer, m.p. 247·5—248°C dec., NMR (CDCl$_3$) $\delta$ 7·1 (m, 16, aromatic H), 4·25 (s, 4, cyclobutane H), 5·7 (s, 4, olefinic H). For C$_{32}$H$_{24}$ (408·5) calculated: 94·08% C, 5·92% H; found: 94·11% C, 6·00% H, m.w. 401.

*Formation of photoadduct* VII. A solution of 1·0 g (4·8 mmol) of *I* and 0·5 g (2·5 mmol) of *III* in cyclohexane (125 ml) was irradiated for 6 h. Filtration of the reaction mixture gave 264 mg of tropone dimer *IV*. Chromatography of the filtrate on a silica gel column, using in succession hexane and hexane–benzene mixtures as eluants, afforded 90 mg of dibenzoheptafulvene dimer *VI* and 398 mg of crude 1 : 1 adduct *VII*, m.p. 210—216°C dec. Two recrystallizations from benzene–hexane furnished pure *VII*, m.p. 217—218°C dec.; NMR (CDCl$_3$) $\delta$ 7·25 (m, 16, aromatic H), 5·7 (s, 2, olefinic H), 4·2 (s, 4, cyclobutane H). For C$_{31}$H$_{22}$O (410·5) calculated: 90·70% C, 5·40% H; found: 90·40% C, 5·42% H; m. w. 410.

*Formation of photoadduct* VIII. Irradiation of a solution of 0·5 g of *I* and 1·0 g of *II* in cyclohexane (125 ml) for 6 h, led to deposition of 0·75 g of a solid mixture which consisted of starting monomers *I* and *II*, ketone dimer *IV* tropilidene dimer *V*, and desired cycloadduct *VIII*. Repeated column chromatographic separation of the crude mixture on silica gel, followed by preparative thin layer chromatography (0·75 mm layer of silica gel eluted with 1 : 1 benzene–hexane) afforded 55 mg (10%) of crude adduct *VIII*, m.p. 285—287°C dec. Recrystallization from benzene–hexane furnished pure *VIII*, m.p. 290—291°C dec., NMR (CDCl$_3$) $\delta$ 7·38 (m, 16, aromatic H), 4·23 (s, 4, cyclobutane H), 3·5 (m, 2, methylene H). Subsequent attempts (recrystallization, chromatography, sublimation) to completely separate *VIII* from unreacted tropone *I* were unproductive. For C$_{30}$H$_{22}$O (398·5) calculated: 90·42% C, 5·56% H; found: 89·52% C, 5·62% H.

*Formation of photoadduct* IX. A solution of 0·5 g of *III* and 0·5 g of *II* in isopropyl alcohol (125 ml) was irradiated for 100 h. Evaporation of the solvent *in vacuo* gave a solid mixture shown by thin layer chromatography to consist of unreacted monomers *II* and *III*, hydrocarbon dimers *V* (20%) and *VI* (31%) and desired adduct *IX*. Chromatography on a column of silica gel (light petroleum as eluant) gave 100 mg of crude *IX*, m.p. 266—269°C dec., which on recrystallization from benzene–hexane afforded an analytical sample of the cycloadduct *IX*, m.p. 273—274°C dec.; NMR (C$_6$D$_6$) $\delta$ 7·11 (m, 16, aromatic H), 4·05 (m. 4, cyclobutane H), 5·41 (s, 2, olefinic H), 4·43 (s, 2, methylene H). For C$_{31}$H$_{24}$ (396·5) calculated: 93·89% C, 6·11% H; found: 93·51% C, 6·13% H.

*Formation of* V *by reduction of* IV. A mixture of 0·5 g (1·2 mmol) of dibenzotropone dimer (*IV*) and 1·5 g (7·2 mmol) of aluminum isopropoxide was heated gradually to 250°C in a micro distillation apparatus and maintained at that temperature until distillation of isopropyl alcohol had ceased. After cooling to room temperature, the residual solid mass was vigorously stirred with 30 ml of dilute hydrochloric acid for 2 h. Filtration afforded 0·5 g of yellow solid which after two recrystallizations from toluene furnished 300 mg of hydrocarbon dimer *V*, m.p. 341—342°C dec. The melting point was not depressed upon admixture with photodimer *V*.

*Formation of* VI *and* VII *by Wittig reaction of* IV. To a suspension of methylenetriphenylphosphorane [prepared by the reaction of phenyllithium with 1·9 g (5 mmol) of triphenylmethylphosphonium iodide] in ether was added dropwise a solution of 1·0 g (2·4 mmol) of dibenzotropone dimer *IV* in 30 ml of dry tetrahydrofuran. The reaction mixture was heated at reflux for one h, allowed to cool and filtered. Evaporation of solvents gave a white solid, m.p. 216—221°C dec., which was subjected to chromatography on a column of neutral alumina. Elution with hexane gave 310 mg of dibenzoheptafulvene dimer (*VI*), m.p. 242—245°C dec. Recrystallization from

ligroin furnished 200 mg of *VI*, m.p. 247—248·5°C dec.; the melting point on admixture with photodimer *VI* was undepressed.

Further elution of the column with 3 : 1 benzene–hexane gave 100 mg of crude *VII*, m.p. 208—212°C dec. Recrystallization from ligroin (60—90°C) gave 85 mg of *VII*, m.p. 215 - 216·5°C dec., shown by mixture melting point determination to be identical to photodimer *VII*.

*Formation of* VIII *by partial reduction of* VI. The partial reduction of diketone *IV* was effected by the procedure described previously for the synthesis of *V*; only one molar equivalent of reducing agent was employed. A mixture of 1·8 g (4·3 mmol) of *IV* and 0·88 g (4·3 mmol) of aluminium isopropoxide gave after the usual workup a mixture of monomers *I* and *II* (formed by thermal decomposition at the reaction temperature employed), unreacted dimer *IV*, completely reduced dimer *V* and the desired cycloadduct *VIII*. Isolation of *VIII* was achieved by repeated chromatographic separations on silica gel. Recrystallization from benzene–hexane afforded 55 mg of *VIII* m.p. 290—291°C dec. The melting point was undepressed upon admixture with photoadduct *VIII*.

*Formation of* IX *by reduction of* VII. A mixture of 200 mg of cycloadduct *VII* and 1·0 g of aluminium isopropoxide was allowed to react in the manner described previously for the synthesis of dimer *V*. Chromatographic separation of the reaction mixture afforded 65 mg of adduct *IX*, m.p. 258—265°C dec. Recrystallization from benzene–hexane afforded a comparison sample of *IX*, m.p. 272—273°C dec., identical in all respects (mixture melting point, tlc mobility, spectral data) with photochemically produced *IX*.

*Thermal decomposition of dimers and adducts.* Each photodimer *IV*— *VI* and photoadduct *VII*— *IX* was heated to its respective melting point and maintained at that temperature for several minutes. Analysis of the melt is given by the following representative examples.

Photodimer *V* was maintained at 345°C for 5 min and the melt allowed to cool. Recrystallization from ligroin gave *II*, m.p. 132—133°C (lit.[1], m.p. 131°C).

Photoadduct *VII* was similarly decomposed at 220°C. Tlc. analysis of the melt indicated the absence of *VII* and the presence of substances with $R_F$ values identical to those of tropone monomer *I* and heptafulvene monomer *II*.

*Ozonolysis of* IV, *formation of* cis,trans,cis-1,2,3,4-*tetracarbomethoxycyclobutane* (X). Ozone was bubbled at a rate of 3 g per h through a suspension of 1·0 g of dibenzotropone dimer *IV* in 100 ml of 90% aqueous acetic acid for 24 h at room temperature. Hydrolysis of the resulting solution at room temperature (24 h) with 10 ml of 30% hydrogen peroxide, followed by evaporation of solvents gave a gummy solid. To a solution of this crude reaction product in 10 ml of anhydrous tetrahydrofuran was added slowly an ethereal solution of diazomethane[15] prepared from 20·6 g of nitrosomethylurea. Evaporation of the solvents yielded 1·0 g of crude product which after chromatography on a silica gel column gave 200 mg of tetraester *X*, m.p. 140 to 144°C. Recrystallization from benzene gave pure *X*, m.p. 143—144°C (lit. 6, m.p. 144—145°C). The melting point upon admixture with an authentic sample of *X* was undepressed.*

*Formation and attempted isomerization of* cis,cis,cis-1,2,3,4-*tetracarbomethoxycyclobutane* (XI). β-Heptacyclene[16] was subjected to identical ozonolysis, esterification and chromatographic conditions described previously for photodimer *IV*. cis,cis,cis-1,2,3,4-tetracarbomethoxycyclobutane (*XI*), m.p. 203—204°C (lit.[7], m.p. 203—205°C) was obtained; no cis,trans,cis-tetraester *X* was detected.

*  A comparison sample of the ester was kindly furnished by Prof. C. W. Griffin.

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